

HIGH-THROUGHPUT METHODS FOR FLAMMABILITY SCREENING OF MULTICOMPONENT POLYMER BLENDS AND NANOCOMPOSITES

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ABSTRACT

A summary of research directed at the development and application of high-throughput methods for multi-component polymer blends and nanocomposites is presented.

KEY WORDS: combinatorial, high-throughput, nanocomposites

1. INTRODUCTION

Flammability performance standards for new materials are most often met through the use of additives. To ensure compliance, complex mixtures containing the polymer resin, stabilizers, processing agents, pigments, and flame retardant additives are formulated, characterized, and tested one at a time. While it is in the interests of the public that flammability testing continues to be a critical component of materials research and development (R&D), there are no guarantees that innovation cycle times can be sufficiently reduced using this approach to respond to the competitive pressures of the global marketplace. The recognition that industry needs more efficient tools for materials R&D has prompted the Building and Fire Research Laboratory (BFRL) at the National Institute of Standards and Technology (NIST) to initiate a program of research directed at the development of high-throughput (or combinatorial) methods for materials flammability research. In this context, we use the term “high-throughput” to refer to a research strategy characterized by conducting many experiments at the same time. By virtue of its inherent efficiency, this approach will provide us with the capability to explore compositional space and thereby develop a better understanding of the interactions between components and their effects on the ultimate performance of these materials. This knowledge can be used by industry to determine optimal compositions with respect to materials flammability and other properties.

Recent work conducted in our laboratory [1,2] has clearly demonstrated that nanocomposites consisting of polymer and aluminosilicate clay are significantly less flammable, as indicated by a reduction in peak heat release rate (HRR), than are immiscible mixtures of these components. This is evident in [Figure 1](#), which compares the HRR curves (measured by oxygen consumption calorimetry) from two polypropylene (grafted with maleic anhydride) nanocomposites to the values obtained from the pure polymer (PPgMa). Since the intensity of a fire involving these materials will be proportional to the peak HRR, the dramatic reduction observed in the nanocomposites (by almost a factor of 4) indicates that they are substantially less flammable than pure PPgMa even though they contain only small amounts of clay (~ 4% or

less). This favorable result is not achieved at the expense of compromising other physical properties. Indeed, in most cases, a dramatic improvement in the mechanical properties of these materials is also realized [3,4]. Preliminary results suggest that it is possible to make these nanocomposites from a wide range of polymers, thereby opening the way for the development of an entirely new generation of low flammability, high performance materials.

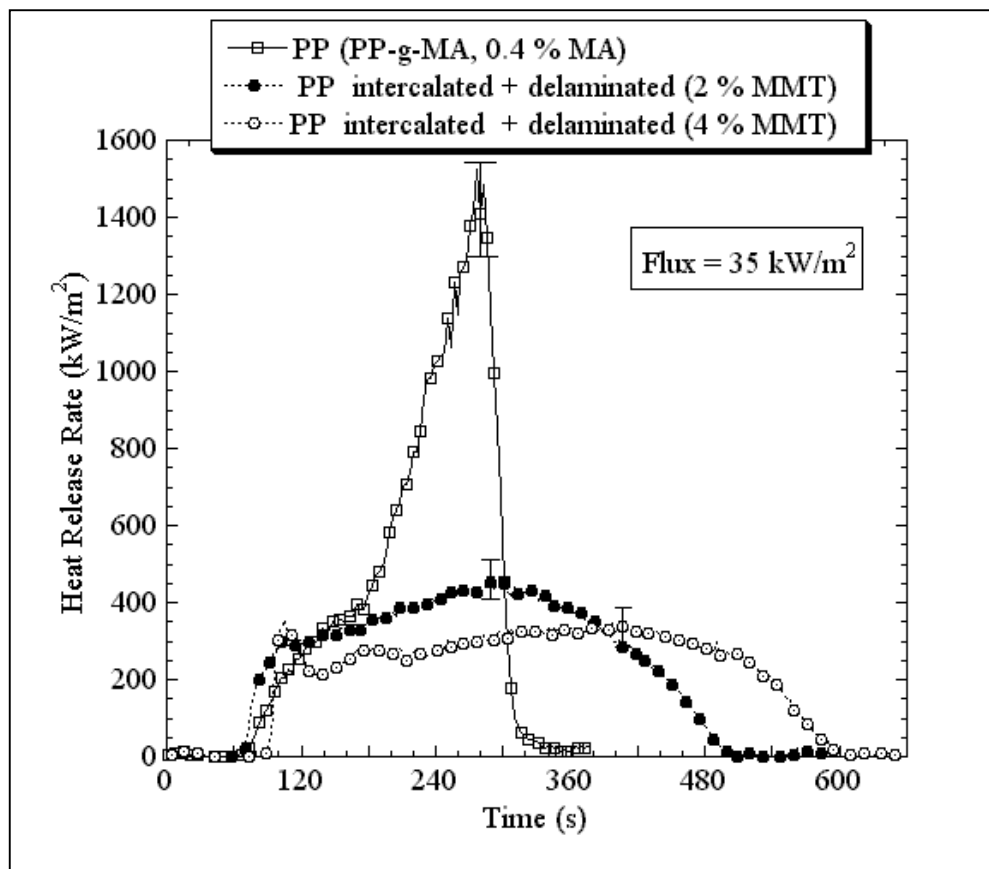
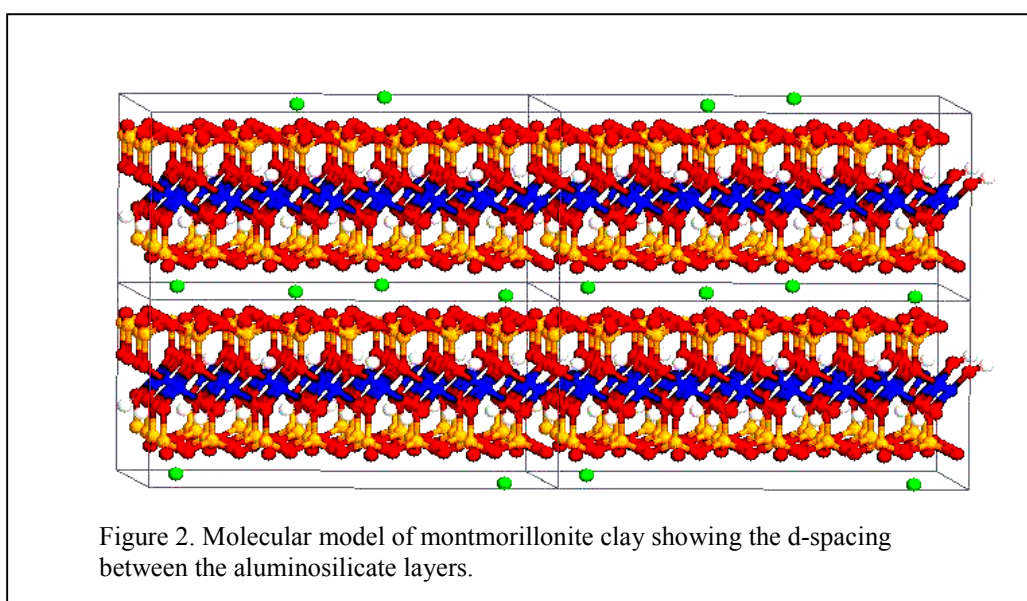


Figure 1. Heat release rates for PPgMa/clay nanocomposites compared to the values obtained for the pure polymer.

Aluminosilicate clays are immiscible in most hydrocarbon polymers. For this reason, it is necessary to treat the clay with a compatibilizer that renders it organophilic. This usually involves the introduction of an organic compound containing a positively charged functional group, such as a quaternary alkylammonium, that can ion exchange with counter-ions associated with the clay. In this way, the ammonium becomes ionically tethered to the clay while the alkyl chain solvates in the polymer. The result of the interaction between the polymer and clay can range from an immiscible mixture to a nano-dispersed composite, depending on the degree of compatibility achieved. With respect to the latter classification, there are two limiting morphologies. Thus, when the compatibility is low, but not so low as to preclude any mixing, the extended polymer chains occupy the gallery spaces between the silicate layers that comprise the clay (Figure 2). The average distance between these layers (d-spacings) increases, but the ordered structure present in original clay is preserved. Consequently, the polymer is viewed as being *intercalated* in the clay. If, on the other hand, there is a high degree of compatibility between the clay and the polymer, the layers delaminate and become dispersed in the polymer.

The interlayer spacings in these *delaminated* (or exfoliated) structures can be on the order of the radius of gyration of the amorphous polymer. In fact, it is very difficult to achieve uniform dispersion and the majority of the nanocomposite materials we have studied in our laboratory contain both intercalated and exfoliated regions.

Many compatibilizers, including the most commonly used alkylammonium compounds, are susceptible to mechanical and thermal degradation that can cause the nanocomposite to ignite at lower temperatures (even though, once ignited, they tend to burn at a much slower rate) than the pure polymer [5,6]. Furthermore, commercial applications of polymer-based materials usually require the addition of plasticizers, curing agents, stabilizers, and pigments, which can cause a further deterioration in their properties. With high-throughput experimentation, we have the opportunity to explore the complex interactions that govern the ultimate performance of these multicomponent materials. The variables of interest are summarized in [Table I](#).



In this paper, we report on the progress we have made in applying high-throughput methods to the formulation, characterization, and flammability screening of multi-component polymer blends and nanocomposites.

Table I. Parameter Space for High-Throughput Experiments on Polymer/Clay Nanocomposites

Polymer	Nano-additive	Counter -Ion	Organic Treatment	Processing Conditions	Other Additives	Flame Retardant
Polyethylene	MMT	Na	Alkylammonium	Temperature	Stabilizers	Phosphate
Polypropylene	Mica	Ca	Imidazolium	Shear	Processing	Halogenated
Polystyrene	Hectorite	Cu	Crown Ether	Residence	UV	Silicon -
Nylon 6	Saponite	Fe	Silated	time	Antioxidant	Based
polyurethane	Laponite		Carboxylate		Fillers	
polymethylmethacrylate	Silica				Pigments	
polyvinylchloride						
polycarbonate						
polyethyleneoxide						
polyethylenevinylacetate						

2. RESULTS

2.1 Parallel Synthesis

Existing technology used for combinatorial chemistry in the pharmaceutical sector can be exploited in making sample libraries of polymer/clay nanocomposites. Here we report on results obtained from our first set of experiments using a parallel reactor equipped with 24 teflon test tubes manufactured by Advanced ChemTech.* The purpose of this investigation was to determine the relative thermal stabilities of polystyrene (PS) composites obtained from clays treated with a series of imidazolium salts. The compatibilizers under investigation differed by the chain lengths of alkyl substituents on the 5th position of the imidazole ring. The preparation of the experimental samples was initiated by adding a small quantity of either propyl, butyl, decyl, or hexadecyl dimethyl imidazolium salt to test tubes containing aqueous suspensions of sodium montmorillonite clay (MMT). In this form, the clay is already delaminated due to favorable interactions with H₂O. Upon introducing the imidazolium salts, the organically treated clays precipitated from the aqueous solutions and the excess water was drained from the reaction vessels. The residual solids were then washed and dissolved in toluene together with the PS resin. Test tubes containing these solutions were heated at temperatures between 25 °C to 60 °C (to determine the effect of temperature on the product) and mixed (by orbital motion) before removing the toluene by vacuum filtration. Some of the samples were exposed to ultrasound from a wand-like source that was inserted directly into the reaction vessels. Thermal gravimetric analyses (TGA) were then performed on the isolated products.

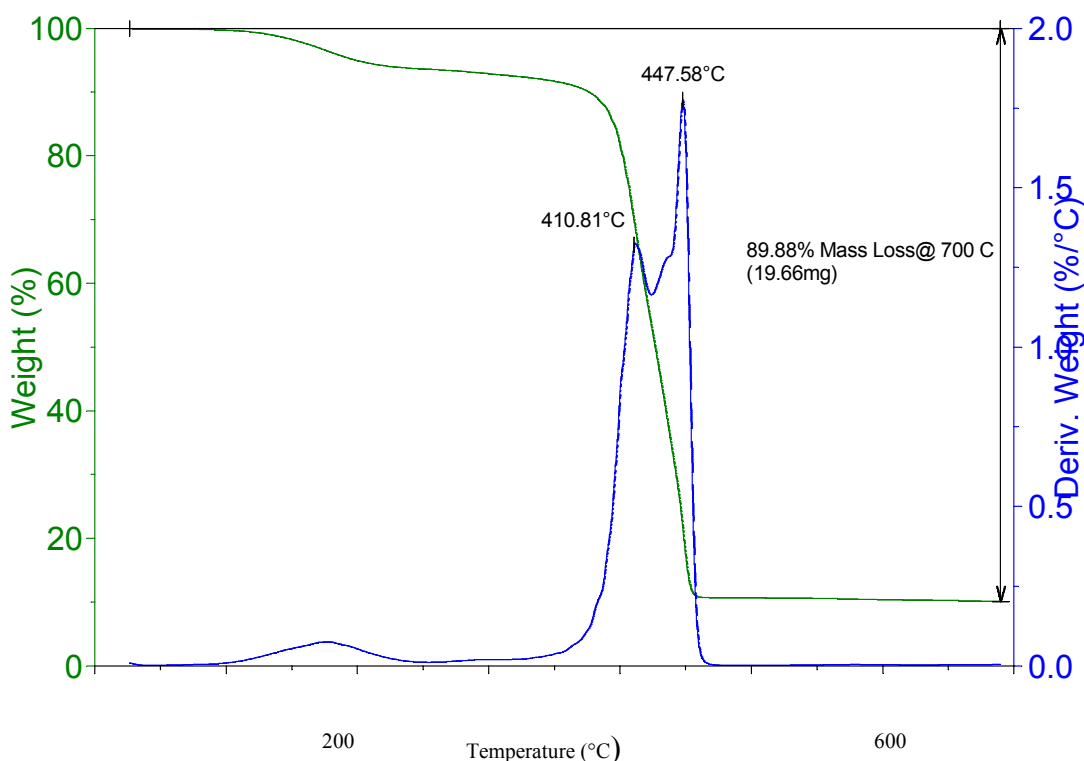


Figure 3. TGA of a PS/MMT sample treated with the hexadecyl dimethyl imidazolium.

* Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by NIST.

A PS/MMT sample, which was treated with the hexadecyl dimethyl imidazolium at 60 °C and sonicated for approximately 30 minutes, gave the best indication that some nanocomposite (as distinguished from an immiscible mixture of clay and polymer where there is no delamination or expansion of the clay layers) was formed. The TGA results for this sample are displayed in Figure 3. The peaks at 411 °C and 446 °C are due to the thermal decompositions of the PS and a PS/clay nanocomposite, respectively. These assignments are supported by the observation that, in the absence of the MMT, PS has a single peak at 414 °C and that the TEM of a sample from this reaction vessel (Figure 4) clearly shows delamination of some of the clay.

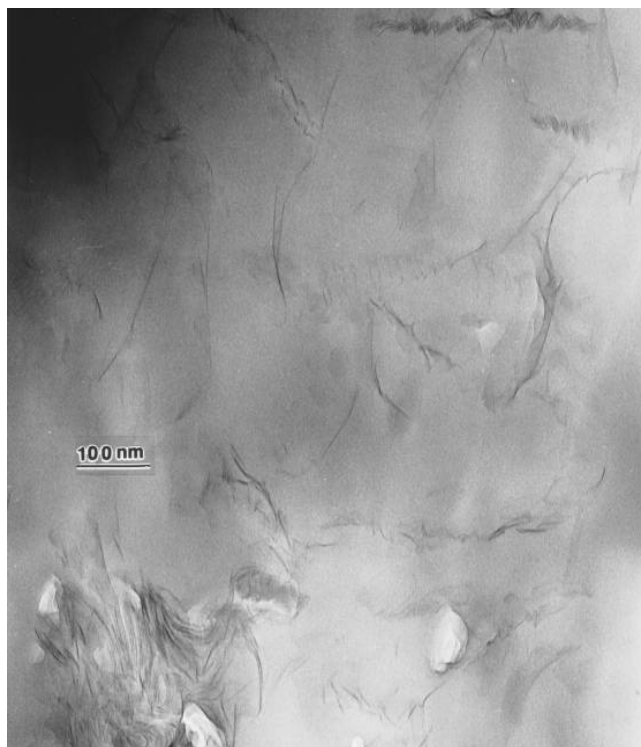


Figure 4. TEM image of PS/clay nanocomposite indicating delamination of some clay layers.

2.2 High-Throughput Flammability Screening

Beginning in the early 1990s, the capabilities for Si micromachining and the demand for low power gas sensing platforms motivated to the fabrication of miniature heating devices. A surface micro-machined microhotplate, pioneered by researchers at NIST [7], can be heated from about 20 °C to 500 °C at rates exceeding 10^6 °C/s. These devices are approximately 100 μm x 100 μm and consist of three functional components (Figure 5): a polysilicon resistor, which generates heat by application of a current, a metal plate for uniform temperature distribution, and four arrow-shaped contact pads.

Previous work conducted by Semancik and others, has demonstrated the use of these microhotplates as microsensors [8]. In this application, a metal oxide film is deposited on the contact pads and the conductance changes resulting from the interaction of gaseous agents and the sensing film are monitored. Rapid temperature-programmed operation (with thermal time constants in the millisecond range), made possible because of the extremely small mass (~ 0.2

μg) of the elements, has been employed to obtain analyte-specific signatures. More recently, these devices have been used as microscale research platforms to study the selectivities and sensitivities of sensing materials [9].

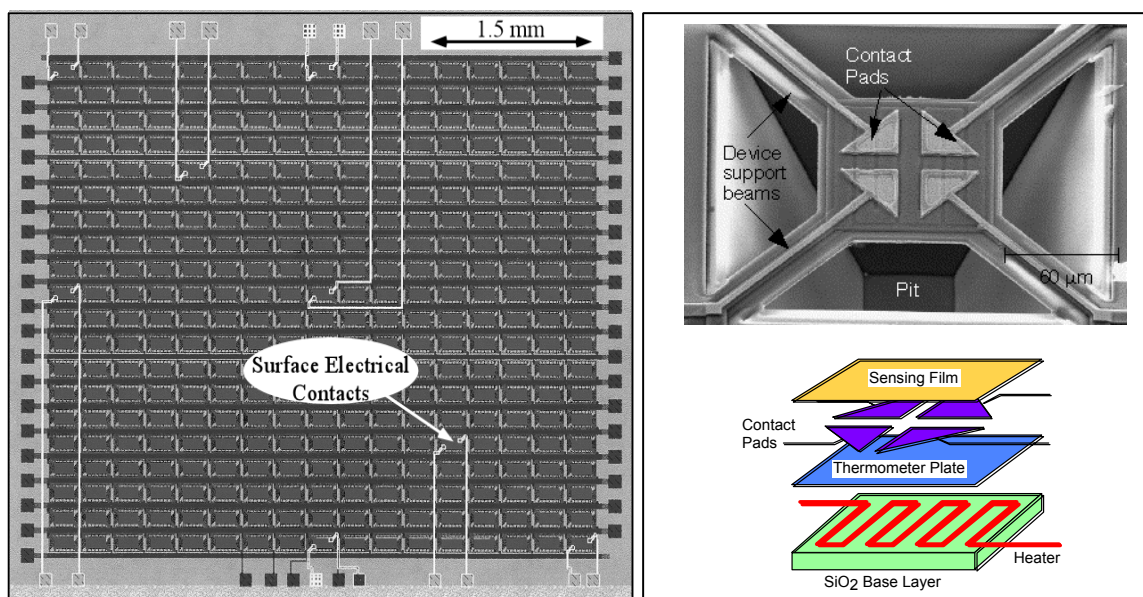


Figure 5. 17x20 element microhotplate array (left) and a magnified image of a single element (right) with a diagram showing the functional components.

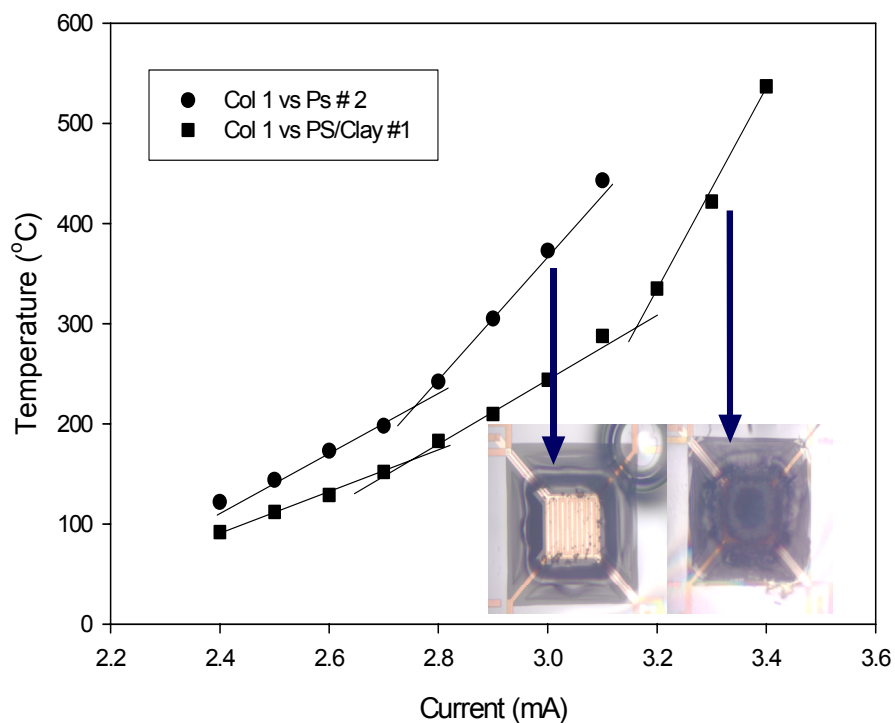


Figure 6. Microhotplate heating curves for PS (circles) and a PS/clay nanocomposite (squares).

We are in the process of adapting microhotplate arrays for high-throughput flammability screening of the polymer/clay nanocomposites. What follows is a summary of the results from our first set of experiments. Samples of PS and PS/clay in toluene were extracted from the reactor and deposited on the microhotplate elements using a micro-pipette fabricated by drawing out the tip of a common medicine dropper. Once deposited, the samples were heated by providing a current ramp to the resistors. The sample temperatures are plotted as functions of the applied current in Figure 6. The PS sample exhibits a transition (indicated by a change in slope), which we think is related to its melt-flow temperature, at about 225 °C. The PS/clay sample has a similar transition at a lower temperature (~ 180 °C), but also shows a second transition at about 320 °C, which may be due to the formation of a char. A comparison of optical micrographs of the PS and PS/clay micro-samples after heating clearly indicate the nanocomposite is more thermally stable than the pure polymer, which is consistent with the TGA results. Thus, the PS appears to have completely gasified by 378 °C, whereas the PS/clay sample is still on the micro-hotplate at 422 °C.

2.3 High-Throughput Characterization

All other things being equal, we expect that the improvement in both the mechanical and flammability properties of polymer/clay nanocomposites will correlate with the dispersion of the clay in the polymer. The usual methods for characterizing dispersion are X-ray diffraction (XRD), from which the interlayer spacings can be determined (as long as the clay retains order along the C axis), and transmission electron microscopy (TEM), which provides a direct image of the clay and polymer (albeit, only in a microscopic region). Unfortunately, these techniques do not provide a quantitative measure of the degree of exfoliation and dispersion and they are difficult to adapt for high-throughput implementation. For this reason, we are directing our efforts to the development of a spectroscopic method based on the use of cationic dyes that can intercalate in the clay. The foundation for this method was established in a recent paper where the effect of intercalation on the UV/VIS absorbance spectra of three cationic dyes was

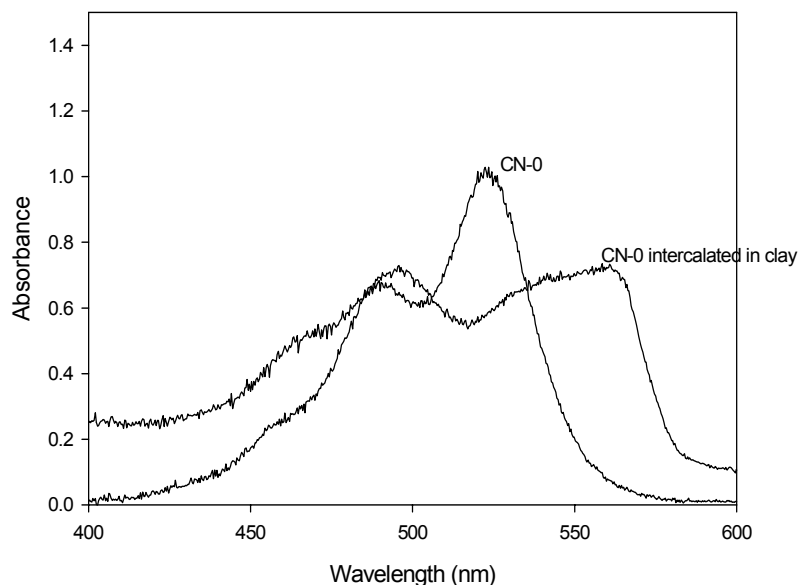


Figure 7. UV/VIS spectra of CN-0 before and after intercalation in montmorillonite clay.

investigated [10]. We reproduced some of the spectra reported in this paper by dipping a fiber optic probe into aqueous solutions containing 1,1'-diethyl-2,2'-cyanine chloride (CN-0) and MMT. These spectra, which took only a few seconds to acquire, are shown in Figure 7. Intercalation of the CN-0 in clay results in a distinct shift in the positions of the peaks. We expect to be able to make use of these differences in quantifying both the concentration of clay in the polymer and the extent to which the layers delaminate.

2.4 Continuous Gradient Extrusion

The parallel synthesis approach described above is well suited to lead-discovery motivated research involving small (~1 g) samples. However, we also need a method for evaluating the performance of experimental formulations under more realistic processing conditions. Our ideas for this are conceptualized in Figure 8 [11]. This device, hereafter called the continuous gradient extruder (CGE), consists of a series of programmable gravimetric feeders capable of producing a compositional gradient in the extruded polymer, infrared and visible sensors that monitor both the concentrations (by quantitative infrared spectroscopy) and degree of dispersion of the additives, and a flammability test method.

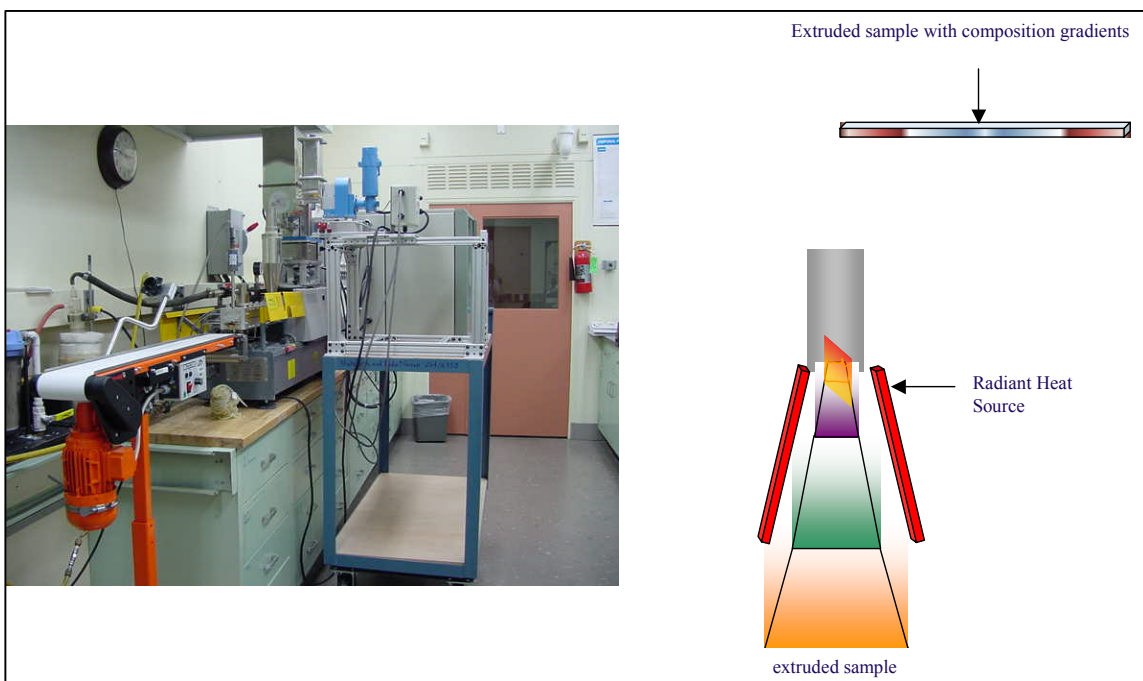


Figure 8. Photograph of our extruder with computer controlled gravimetric feeders (left) and a picture that depicts the experimental design for flammability screening of compositionally graded materials.

A compositionally graded sample containing ammonium polyphosphate (APP) and pentaerythritol (PER) in polystyrene was produced in the CGE and burned in our horizontal ignition flammability test (HIFT) device under a constant flux of $(16.8 \pm 0.4) \text{ kW/m}^2$. The sample was a strip (approximately 1.5 m long, 0.007 m wide and 0.002 m thick) consisting of PS blended with varying amounts of a 3:1 mixture of APP and PER. We attempted to create a linear concentration gradient (from $C = 0\%$ to $C = 30\%$ additive by mass) by increasing the rate of feed from the hopper containing the mixture of APP and PER linearly with time.

Progression of Flame Front

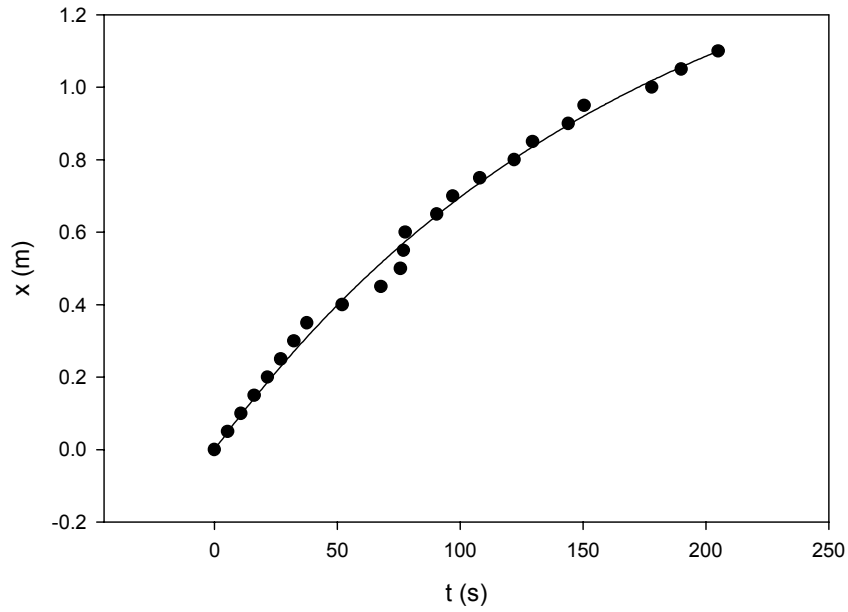


Figure 9. The progression of the flame front as a function of time measured for the PS/APP/PER gradient. The solid line was obtained by fitting the experimental data (circles) to a hypothetical function derived on the basis of assumptions stated in the text.

Progression of the Flame Front with Time

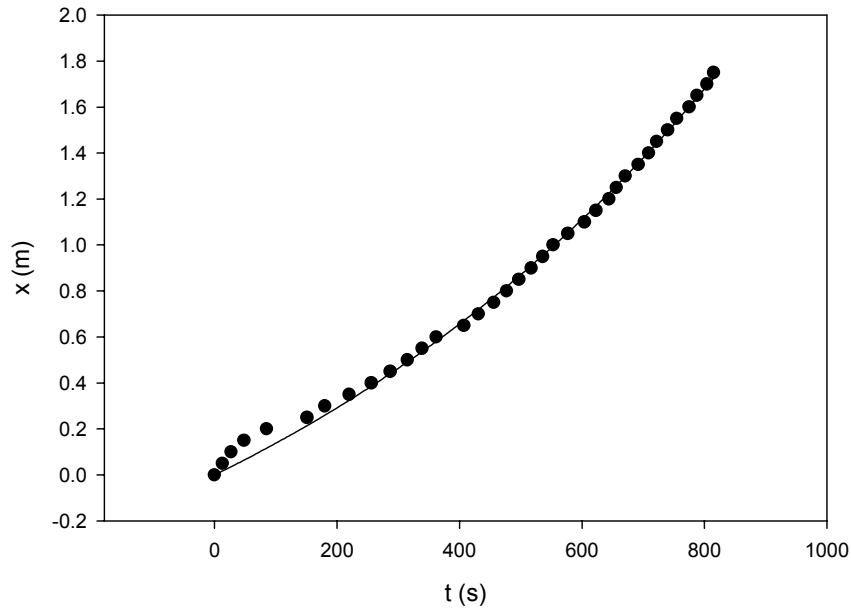


Figure 10. The progression of the flame front as a function of time measured for PS/clay gradient. The solid line was obtained by fitting the experimental data (circles) to a hypothetical function derived on the basis of assumptions stated in the text.

The flame velocities were measured by pulling the extruded strip through a 300 mm heating zone such that the flame front remained at a fixed position. The results are plotted in [Figure 9](#). The data (t) was collected at 0.050 m intervals, which were marked off on the strip, with the initial point (at $x = 0$) corresponding to the pure polymer ($C = 0\%$ at $x = 0$). The solid line was obtained by fitting the experimental data to a hypothetical function (exponential) that was derived by assuming a linear dependence between flame velocity and additive concentration, which was also assumed to decrease linearly with distance. The validity of these assumptions is supported by the fact that this function does a good job of representing the experimental data. The derivative of the function in [Figure 9](#) is a linear function of x (or $C = ax$) with a negative slope indicating a reduction in the flame velocity with increasing concentration of additive as expected.

Comparable data was collected for a PS/clay strip with an approximately linear concentration gradient of clay varying from 0 % to about 14 % by mass. In this case, the flame velocities were observed to accelerate with increasing clay concentration ([Figure 10](#)), suggesting that the presence of the clay actually enhances the spread of flames over the surface of this material. This observation is consistent with our previous observation that polymer/clay nanocomposites ignite at lower temperatures (even though, once ignited, they tend to burn with a lower HRR) than the pure polymer, since lower ignition temperatures facilitate flame spread. Eventually, we would like to make simultaneous measurements of both flame velocity and heat release to determine the optimal composition, which results in the best compromise between flame spread and HRR.

3. SUMMARY AND CONCLUSIONS

An overview of the research directed at the development and application of high-throughput methods for multi-component polymer blends and nanocomposites that is currently underway in the Building and Fire Research Laboratory was presented. Substantial progress has been made in the parallel synthesis, extrusion, characterization, and flammability screening of these materials. We anticipate that our approach of combining high-throughput experimentation with nano-technology will yield new insights into the ways that components interact to determine the ultimate properties of complex materials.

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